

# Hydrogen Isotope Disproportionation and Fractionation Equilibria in $\text{H}_2\text{O}-\text{D}_2\text{O}$ Solvent System. I. Fractionation of Deuterium between Trihalomethanes and Water

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The equilibrium constant of the isotope disproportionation reaction between  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  in liquid phase has been calculated from isotope fractionation factor measurements carried out with trichloromethane, bromodichloromethane and tribromomethane in different  $\text{H}_2\text{O}-\text{D}_2\text{O}$  mixtures. A value of 3.76(6) was obtained for the equilibrium constant  $K(\text{HDO})^2$ . The statistical value is  $K(\text{HDO})^2=4$ . The effect of a breakdown of the postulate of the geometric mean on the isotope fractionation equilibria of substrates with one exchangeable hydrogen is discussed.

The isotope disproportionation equilibrium  $\text{H}_2\text{O} + \text{D}_2\text{O} = 2 \text{HDO}$  is important in the treatment of solvent isotope effects in mixtures of  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$ . In the simple theory of solvent isotope effects<sup>1-3</sup> one of the assumptions made is that the postulate of the geometric mean<sup>4</sup> (PGM) governs the isotope disproportionation equilibria involved. According to the PGM, the equilibrium constant of the reaction  $\text{H}_2\text{O} + \text{D}_2\text{O} = 2 \text{HDO}$  has already at ordinary temperatures its classical value 4, which is determined by symmetry considerations alone. By means of the PGM the calculations can be appreciably simplified. The correct value of the equilibrium constant of the isotope disproportionation reaction of water both in gas and liquid phase has occupied the mind of scientists ever since the discovery of deuterium.<sup>5-21</sup> It has been shown that the PGM does not hold for the mixtures of  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$ . A breakdown of the PGM in the isotope disproportionation reaction of water has straightforward consequences for the isotope fractionation equilibria in the  $\text{H}_2\text{O}-\text{D}_2\text{O}$  solvent system. In

particular, knowledge of the exact value of the equilibrium constant is of great importance for the theory of solvent deuterium isotope effects. In spite of the importance of the isotope disproportionation equilibrium of liquid water there has, however, been quite a lot of discordance in the values of the equilibrium constant of this reaction. Besides, most of the experimental studies carried out are associated with the gas phase. The aim of this work was to acquire more experimental information about the hydrogen isotope disproportionation in the liquid phase and about the effect of a breakdown of the PGM on the isotope fractionation equilibria in the  $\text{H}_2\text{O}-\text{D}_2\text{O}$  solvent system. An indirect method was used to determine the value of equilibrium constant of the isotope disproportionation reaction of liquid water. The method is based on the fact that for the deuterium isotope fractionation in a substrate with only one exchangeable hydrogen, the deviations from the PGM are confined to the solvent water and are reflected in the dependence of the fractionation factor upon the deuterium isotope mol fraction of water.

## EXPERIMENTAL

*Materials.* Trichloromethane (E. Merck AG, *pro analysi*) was used as received. Bromodichloromethane (EGA-Chemie KG) and tribromomethane (E. Merck AG, *reinst*) were distilled once before use.

Deuteriotrichloromethane, deuteriobromodichloromethane and deuteriotribromomethane were prepared by shaking trihalomethane and deuterium oxide at 25 °C with NaOD as catalyst. The reactions were followed by <sup>1</sup>H NMR spectroscopy (a 60 MHz

Perkin-Elmer Model R 10 spectrometer). The deuterium oxide portions "worsened" in the reactions were replaced by fresh portions of  $D_2O$ , the procedure being repeated five times in all. In each portion of  $D_2O$  the deuterium excess over trihalomethane was about threefold. The deuterio-trihalomethanes were dried over anhydrous  $MgSO_4$  and distilled. The final degree of deuteration was determined by  $^1H$  NMR spectroscopy and was found to be 99.7% for the deuterio-trichloromethane, 99.1% for the deuterio-bromodichloromethane and 98.9% for the deuterio-tribromomethane.

The deuterium oxide used in the experiments was a product of Norsk Hydro-elektrisk Kvaestofaktieselskab. The deuterium isotope mol fraction of  $D_2O$  was reported to be 0.998.

For the equilibration experiments the sodium hydroxide-sodium deuterioxide solutions, in which the deuterium isotope mol fraction of water varied between 0.1-0.9, were usually prepared by weight from pure light and heavy water, adding a suitable amount of NaOL (L=H, D) just before the equilibrations. When calculating the solvent deuterium isotope mol fraction of each solution, the increase of  $H_2O$  or  $D_2O$  coming from the added catalyst solution was taken into consideration. For the equilibrations of trichloromethane, aqueous NaOL-solutions were prepared by mixing aqueous NaOH- and NaOD-solutions in suitable volumetric ratios. To calculate the deuterium isotope mol fraction of water in the mixed solutions, the densities of the NaOH- and NaOD-solutions were determined. The aqueous sodium hydroxide solution was prepared from a standard Titrisol solution (E. Merck AG) by dilution with distilled water. The corresponding sodium deuterioxide solution was made by diluting a stock solution of NaOD with deuterium oxide. The stock solution was prepared by dissolving metallic sodium in deuterium oxide under toluene in a separating funnel. The base concentration of the sodium deuterioxide solution was determined by titration with a known acid solution.

For IR-measurements the reference solutions of trihalomethanes in  $CCl_4$  were prepared by adding suitable amounts of  $CHX_3$  and  $CDX_3$  (X=Cl, Br) to 2  $cm^3$  portions of carbon tetrachloride with the aid of an Agla micrometer syringe. The total volume of  $CLX_3$  in each solution was 0.05-0.06  $cm^3$ . The mol fraction of  $CDX_3$  in the  $CLX_3$ -solutions varied between 0-0.997. The molar volumes of a trihalomethane and the corresponding deuterio-trihalomethane were assumed to be equal.

*Equilibration experiments.* In the equilibrations the substrate-catalyst-water mixtures were shaken in 50  $cm^3$  separating funnels surrounded by a jacket for water circulation. The system was held at a

constant temperature of 25.0 °C within  $\pm 0.1$  °C with water circulating from a Lauda thermostat. The time of equilibration was maintained about ten times longer than the time that was found necessary just to attain the equilibrium. In the equilibrations the suitable concentration of catalyst was in the range 0.001-0.01  $mol\ dm^{-3}$ , the volume of catalyst-water solution was 40  $cm^3$ , the amount of substrate varied in the range of 0.00067-0.0031 mol and the time of equilibration was between 1-2 h depending on the trihalomethane. After the equilibrium was reached, 10  $cm^3$  samples were taken from the equilibrium mixtures by means of a semiautomatic pipette. The samples were transferred to 25  $cm^3$  separating funnels containing an acid solution for neutralization of the sample and carbon tetrachloride (1  $cm^3$ ) for extraction of the equilibrated substrate. From each equilibrium mixture 3-10 samples were taken. After extraction the deuterium content of the substrate was determined by IR measurements.

*IR measurements.* The measurements were made with a Perkin-Elmer Model 180 IR spectrophotometer using sealed KBr cells of a fixed path length of 0.1 mm. Before the IR analysis the extracts from the equilibrium mixtures were dried over anhydrous  $MgSO_4$ . The spectra of the extracts were recorded immediately after the spectra of the reference solutions. The characteristic absorption peaks used in the analysis were those arising from the C-H and C-D deformation vibrations of the trihalomethanes: 1213 and 907  $cm^{-1}$  for  $CLCl_3$ , 1205, 1164, 898 and 866  $cm^{-1}$  for  $CLCl_2Br$  and 1140, 860 and 845  $cm^{-1}$  for  $CLBr_3$ . For each of the three trihalomethanes examined in this work, a good linear correlation was found to exist between the

Table 1. Mol ratios of deuterium and protium in trichloromethane equilibrated in different  $H_2O$ - $D_2O$  mixtures and the experimental fractionation factors  $\phi'(CHCl_3)$  at 298.2 K.

$x(D;L_2O)^a$	$\frac{n(D;CLCl_3)_b}{n(H;CLCl_3)}$	$\phi'(CHCl_3)^b$
0.0993	0.1290(5)	1.171(5)
0.199	0.2751(13)	1.109(6)
0.298	0.4762(16)	1.120(4)
0.398	0.7284(7)	1.102(1)
0.498	1.086(7)	1.097(7)
0.597	1.634(8)	1.102(6)
0.697	2.455(11)	1.067(5)
0.797	4.42(2)	1.126(6)
0.897	9.49(16)	1.091(19)

<sup>a</sup>  $x(D;L_2O)$  is the deuterium isotope mole fraction of water. <sup>b</sup> Mean values of 8-10 determinations with standard errors of mean.

Table 2. Mol ratios of deuterium and protium in bromodichloromethane equilibrated in different  $\text{H}_2\text{O}-\text{D}_2\text{O}$  mixtures and the experimental fractionation factors  $\phi'(\text{CHCl}_2\text{Br})$  at 298.2 K.

$x(\text{D};\text{L}_2\text{O})^a$	$\frac{n(\text{D};\text{CLCl}_2\text{Br})_b}{n(\text{H};\text{CLCl}_2\text{Br})}$	$\phi'(\text{CHCl}_2\text{Br})^b$
0.103	0.1338(7)	1.165(6)
0.204	0.2830(18)	1.104(7)
0.284	0.4331(12)	1.092(3)
0.401	0.715(3)	1.068(4)
0.475	0.955(3)	1.056(4)
0.610	1.672(11)	1.069(7)
0.699	2.54(2)	1.093(8)
0.807	4.46(4)	1.067(8)
0.897	9.47(11)	1.088(12)

<sup>a</sup>  $x(\text{D};\text{L}_2\text{O})$  is the deuterium isotope mol fraction of water. <sup>b</sup> Mean values of 8 determinations with standard errors of mean.

Table 3. Mol ratios of deuterium and protium in tribromomethane equilibrated in different  $\text{H}_2\text{O}-\text{D}_2\text{O}$  mixtures and the experimental fractionation factors  $\phi'(\text{CHBr}_3)$  at 298.2 K.

$x(\text{D};\text{L}_2\text{O})^a$	$\frac{n(\text{D};\text{CLBr}_3)_b}{n(\text{H};\text{CLBr}_3)}$	$\phi'(\text{CHBr}_3)^b$
0.105	0.1266(7)	1.079(5)
0.108	0.1301(17)	1.074(13)
0.202	0.274(3)	1.081(9)
0.214	0.291(2)	1.070(7)
0.316	0.488(6)	1.056(11)
0.333	0.527(9)	1.056(16)
0.397	0.684(3)	1.039(4)
0.402	0.700(6)	1.041(8)
0.500	1.029(4)	1.029(4)
0.506	1.057(5)	1.032(5)
0.599	1.534(6)	1.027(4)
0.601	1.554(6)	1.031(3)
0.693	2.308(14)	1.023(6)
0.704	2.439(13)	1.025(5)
0.800	4.128(7)	1.032(2)
0.802	4.175(19)	1.031(3)
0.897	8.96(8)	1.028(8)

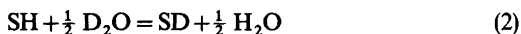
<sup>a</sup>  $x(\text{D};\text{L}_2\text{O})$  is the deuterium isotope mol fraction of water. <sup>b</sup> Mean values of 3–4 determinations with standard errors of mean.

mol fractions of  $\text{CDX}_3$  and the absorbances measured from the spectra of the reference solutions. The correlation coefficients for the straight lines were in the range of 0.9953–0.9999. The results from the equilibrations of the trihalomethanes are listed in Tables 1–3.

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## DISCUSSION

*Calculation of  $K(\text{HDO})^2$ .* When a substrate SH containing one exchangeable hydrogen is dissolved in water of arbitrary deuterium content, the following equilibria are set up: disproportionation equilibrium (1) between isotopically different waters, isotopic fractionation equilibrium (2) between the substrate and the solvent water, and isotopic exchange equilibria (3) and (4), which are not independent ones, but can be presented by combinations of equilibria (1) and (2).



In the following approach it is assumed that in the expressions of equilibrium constants the activities can be replaced by mol fractions. The equilibrium constants of the equilibria (1) and (2) are expressed by eqns. (5) and (6). The fractionation factor  $\phi'(\text{SH})$ ,

$$K(\text{HDO})^2 = \frac{x(\text{HDO})^2}{x(\text{H}_2\text{O})x(\text{D}_2\text{O})} \quad (5)$$

$$\phi'(\text{SH}) = \frac{x(\text{SD})}{x(\text{SH})} \left[ \frac{x(\text{H}_2\text{O})}{x(\text{D}_2\text{O})} \right]^{\frac{1}{2}} \quad (6)$$

which is an experimentally determinable quantity, is defined according to eqn. (7), where  $n$  is the amount of deuterium or protium in SL or  $\text{L}_2\text{O}$ ,  $\text{L} = \text{H}, \text{D}$  and  $x(\text{D};\text{L}_2\text{O})$  is the deuterium isotope mol fraction of solvent water. In terms of mol fractions of isotopic water species, the deuterium isotope mol fraction of water can be expressed by eqn. (8). Using eqn. (8) and the fact that  $x(\text{D}_2\text{O}) + x(\text{HDO}) + x(\text{H}_2\text{O}) = 1$ , eqns. (9) and (10) are obtained for  $x(\text{HDO})$  and  $x(\text{H}_2\text{O})$ . When equations (5), (9) and (10) are solved

$$\phi'(\text{SH}) = \frac{n(\text{D};\text{SL})}{n(\text{H};\text{SL})} \cdot \frac{n(\text{D};\text{L}_2\text{O})}{n(\text{H};\text{L}_2\text{O})} = \frac{x(\text{SD})}{x(\text{SH})} \times$$

$$\frac{1 - x(\text{D};\text{L}_2\text{O})}{x(\text{D};\text{L}_2\text{O})} \quad (7)$$

$$x(\text{D};\text{L}_2\text{O}) = x(\text{D}_2\text{O}) + \frac{1}{2}x(\text{HDO}) \quad (8)$$

$$x(\text{HDO}) = 2[x(\text{D};\text{L}_2\text{O}) - x(\text{D}_2\text{O})] \quad (9)$$

$$x(\text{H}_2\text{O}) = 1 - 2x(\text{D};\text{L}_2\text{O}) + x(\text{D}_2\text{O}) \quad (10)$$

$$\phi(\text{SH}) = \phi'(\text{SH}) \frac{x(\text{D};\text{L}_2\text{O})}{1-x(\text{D};\text{L}_2\text{O})} \times \sqrt{\frac{2[1-x(\text{D};\text{L}_2\text{O})][4-K(\text{HDO})^2] + K(\text{HDO})^2 - \sqrt{F\{K(\text{HDO})^2; x(\text{D};\text{L}_2\text{O})\}}}{2x(\text{D};\text{L}_2\text{O})[4-K(\text{HDO})^2] + K(\text{HDO})^2 - \sqrt{F\{K(\text{HDO})^2; x(\text{D};\text{L}_2\text{O})\}}}} \quad (11)$$

where  $F\{K(\text{HDO})^2; x(\text{D};\text{L}_2\text{O})\} = K(\text{HDO})^4 + 4K(\text{HDO})^2[4-K(\text{HDO})^2]x(\text{D};\text{L}_2\text{O})[1-x(\text{D};\text{L}_2\text{O})]$

simultaneously, the mol fractions of the three isotopic water species are obtained in terms of  $K(\text{HDO})^2$  and  $x(\text{D};\text{L}_2\text{O})$ . The expressions for these mol fractions together with eqns. (6) and (7) lead to eqn. (11) for the computation of the equilibrium constants  $K(\text{HDO})^2$  and  $\phi(\text{SH})$ .\*

The results obtained when the experimental data from Tables 1–3 are applied to eqn. (11) are listed in Table 4. The calculations were performed with a UNIVAC 1108 computer. The mean of the three  $K(\text{HDO})^2$  values from Table 4 is  $K(\text{HDO})^2 = 3.76(6)$ . When this value is used for the equilibrium constant of reaction (1), values for the mol fractions of the different water species in the water of the deuterium isotope mol fraction  $x(\text{D};\text{L}_2\text{O})$ , listed in Table 5, are obtained.

*Effect of Value of  $K(\text{HDO})^2$  on  $\phi(\text{SH})$ .* All equilibria described by (2) contain the ratio  $[x(\text{D}_2\text{O})/x(\text{H}_2\text{O})]^\ddagger$ , cf. eqn. (6). If the PGM were to

Table 4. Equilibrium constants of the isotope disproportionation reaction  $\text{H}_2\text{O} + \text{D}_2\text{O} = 2 \text{HDO}$ ,  $K(\text{HDO})^2$ , and isotope fractionation reaction  $\text{SH} + \frac{1}{2} \text{D}_2\text{O} = \text{SD} + \frac{1}{2} \text{H}_2\text{O}$ ,  $\phi(\text{SH})$ , in the liquid state at 298.2 K.

SH	$\phi(\text{SH})$	$K(\text{HDO})^2$	Data in Table
$\text{CHCl}_3$	1.107(7)	3.79(7)	1
$\text{CHCl}_2\text{Br}$	1.083(9)	3.77(7)	2
$\text{CHBr}_3$	1.041(3)	3.73(5)	3

Table 5. Values for mol fractions of different water species in water of the deuterium isotope mol fraction  $x(\text{D};\text{L}_2\text{O})$  when  $K(\text{HDO})^2 = 3.76$ .

$x(\text{D};\text{L}_2\text{O})$	$x(\text{H}_2\text{O})$	$x(\text{HDO})$	$x(\text{D}_2\text{O})$
0.0	1.0000	0.0000	0.0000
0.10	0.8105	0.1790	0.0105
0.20	0.6416	0.3168	0.0416
0.30	0.4927	0.4145	0.0927
0.40	0.3636	0.4729	0.1636
0.50	0.2539	0.4923	0.2539
0.60	0.1636	0.4729	0.3636
0.70	0.0927	0.4145	0.4927
0.80	0.0416	0.3168	0.6416
0.90	0.0105	0.1790	0.8105
1.00	0.0000	0.0000	1.0000

be valid in regard to the  $\text{H}_2\text{O}-\text{D}_2\text{O}$  mixtures, the ratio of the mol fractions could be expressed by eqn. (12). Actually the right side of eqn. (12) must be expressed by eqn. (13), where  $x(\text{HDO}) = K(\text{HDO}) \times [x(\text{H}_2\text{O})x(\text{D}_2\text{O})]^\ddagger$ . Solving the quadratic equation that results from eqn. (13), an exact equation (14) is obtained for the ratio  $[x(\text{D}_2\text{O})/x(\text{H}_2\text{O})]^\ddagger$ .

$$\left[ \frac{x(\text{D}_2\text{O})}{x(\text{H}_2\text{O})} \right]^\ddagger = \frac{x(\text{D};\text{L}_2\text{O})}{1-x(\text{D};\text{L}_2\text{O})} \quad (12)$$

$$\frac{x(\text{D};\text{L}_2\text{O})}{1-x(\text{D};\text{L}_2\text{O})} = \frac{2x(\text{D}_2\text{O}) + x(\text{HDO})}{2x(\text{H}_2\text{O}) + x(\text{HDO})} \quad (13)$$

\* A referee has pointed out that eqn. (11) can be simplified to

$$\phi(\text{SH}) = \phi'(\text{SH}) \left\{ \frac{\sqrt{[2x(\text{D};\text{L}_2\text{O})-1]^2 K(\text{HDO})^2 + 16x(\text{D};\text{L}_2\text{O})[1-x(\text{D};\text{L}_2\text{O})]} - [2x(\text{D};\text{L}_2\text{O})-1]K(\text{HDO})}{4[1-x(\text{D};\text{L}_2\text{O})]} \right\}$$

The computations have not been repeated with this version since it was found that the above equation gives the same values of  $K(\text{HDO})^2$  and  $\phi(\text{SH})$  as those obtained from computations with eqn. (11).

$$\left[\frac{x(\text{D}_2\text{O})}{x(\text{H}_2\text{O})}\right]^{\ddagger} = \frac{[2x(\text{D};\text{L}_2\text{O}) - 1]K(\text{HDO})}{4[1 - x(\text{D};\text{L}_2\text{O})]} + \frac{\sqrt{[2x(\text{D};\text{L}_2\text{O}) - 1]^2 K(\text{HDO})^2 + 16x(\text{D};\text{L}_2\text{O})[1 - x(\text{D};\text{L}_2\text{O})]}}{4[1 - x(\text{D};\text{L}_2\text{O})]} \quad (14)$$

$$\left[\frac{x(\text{D}_2\text{O})}{x(\text{H}_2\text{O})}\right]_{\text{real}}^{\ddagger} = \gamma \left[\frac{x(\text{D}_2\text{O})}{x(\text{H}_2\text{O})}\right]_{\text{PGM}}^{\ddagger} = \gamma \frac{x(\text{D};\text{L}_2\text{O})}{1 - x(\text{D};\text{L}_2\text{O})} \quad (15)$$

$$\gamma = \frac{[2x(\text{D};\text{L}_2\text{O}) - 1]K(\text{HDO})}{4x(\text{D};\text{L}_2\text{O})} + \frac{\sqrt{[2x(\text{D};\text{L}_2\text{O}) - 1]^2 K(\text{HDO})^2 + 16x(\text{D};\text{L}_2\text{O})[1 - x(\text{D};\text{L}_2\text{O})]}}{4x(\text{D};\text{L}_2\text{O})} \quad (16)$$

$$\gamma = [-0.06144(12)]x(\text{D};\text{L}_2\text{O}) + 1.03086(7) \\ (r = -0.99997) \quad (17)$$

$$\left[\frac{x(\text{D}_2\text{O})}{x(\text{H}_2\text{O})}\right]^{\ddagger} = [1.03086 - 0.06144x(\text{D};\text{L}_2\text{O})] \times \\ \frac{x(\text{D};\text{L}_2\text{O})}{1 - x(\text{D};\text{L}_2\text{O})} \quad (18)$$

To find out direct deviations from the PGM, it is convenient to express the ratio  $[x(\text{D}_2\text{O})/x(\text{H}_2\text{O})]^{\ddagger}$  in the form of eqn. (15) in which the coefficient  $\gamma$  for different values of  $x(\text{D};\text{L}_2\text{O})$  can be calculated from eqn. (16). Applying then the method of linear least squares to values  $[x(\text{D};\text{L}_2\text{O}), \gamma]$ , an expression (17) is obtained for the coefficient  $\gamma$ . The exact equation (14) can thus be expressed in an approximate form (18), which, when compared with eqn. (12), shows direct deviations from the PGM with different values for  $x(\text{D};\text{L}_2\text{O})$ . Combining eqns. (6), (7) and (18), a relationship (19) is obtained between the experimentally determinable fractionation factor  $\phi'(\text{SH})$  and the real fractionation factor  $\phi(\text{SH})$ .

$$\phi'(\text{SH})/\phi(\text{SH}) = 1.03086 - 0.06144x(\text{D};\text{L}_2\text{O}) \quad (19)$$

The ratio  $\phi'(\text{SH})/\phi(\text{SH})$  is independent of the size of the fractionation factor itself and thus it presents the dependence of the fractionation factor  $\phi'(\text{SH})$  of any substrate of type SH on the deuterium content of solvent water. The correction of  $\phi'(\text{SH})$  to obtain  $\phi(\text{SH})$  is given by  $1/[1.03086 - 0.06144x(\text{D};\text{L}_2\text{O})]$  varying from 0.970 at  $x(\text{D};\text{L}_2\text{O})=0$  to 1.032 at  $x(\text{D};\text{L}_2\text{O})=1$ , i.e., 6% over the whole range of  $x(\text{D};\text{L}_2\text{O})$ .

When  $x(\text{D};\text{L}_2\text{O})=0.5$ , the ratio  $[x(\text{D}_2\text{O})/x(\text{H}_2\text{O})]^{\ddagger} = 1$  whether the PGM is valid or not. Thus the fractionation factor  $\phi'(\text{SH})$  measured

in equimolar mixtures of  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  should be quite close to the equilibrium constant  $\phi(\text{SH})$ . Also the mean value of  $\phi'(\text{SH})$ , when measurements of  $\phi'(\text{SH})$  are carried out evenly over the whole range of  $x(\text{D};\text{L}_2\text{O})$ , should be only slightly different from  $\phi(\text{SH})$ . The mean values of the experimental fractionation factors  $\phi'(\text{CHX}_3)$  calculated from the values in Tables 1–3 are  $\phi'(\text{CHCl}_3)=1.109(10)$ ,  $\phi'(\text{CHCl}_2\text{Br})=1.089(11)$  and  $\phi'(\text{CHBr}_3)=1.044(5)$ . The values of  $\phi'(\text{CHX}_3)$  seem to be quite close to the real  $\phi(\text{CHX}_3)$  values (Table 4). The same cannot be said about the values of  $\phi'(\text{CHX}_3)$  measured at solvent deuterium isotope mol fractions of about 0.5:  $\phi'(\text{CHCl}_3)=1.097(7)$  at  $x(\text{D};\text{L}_2\text{O})=0.498$ ,  $\phi'(\text{CHCl}_2\text{Br})=1.056(4)$  at  $x(\text{D};\text{L}_2\text{O})=0.475$  and  $\phi'(\text{CHBr}_3)=1.029(4)$  at  $x(\text{D};\text{L}_2\text{O})=0.500$  and  $\phi'(\text{CHBr}_3)=1.032(5)$  at  $x(\text{D};\text{L}_2\text{O})=0.506$ . Taking into account the scattering in the measured  $\phi'(\text{CHX}_3)$  values, it is clear that the correction for  $\phi'(\text{SH})$  using eqn. (19) will be relevant only when the experimental data are sufficiently accurate.

$$\left[\frac{x(\text{D}_2\text{O})}{x(\text{H}_2\text{O})}\right]^{\ddagger} = \frac{x(\text{D};\text{L}_2\text{O})[1 - x(\text{D};\text{L}_2\text{O}) + \frac{1}{2}K(\text{HDO})^2 x(\text{D};\text{L}_2\text{O})]}{[1 - x(\text{D};\text{L}_2\text{O})] \cdot \frac{1}{2}K(\text{HDO})} \quad (20)$$

Albery and Davies<sup>22</sup> derived an approximate eqn. (20) for small departures from the PGM when  $\frac{1}{2}K(\text{HDO})$  is near unity. When  $K(\text{HDO})^2$  is fixed at 3.76, which is the value obtained in this work, the approximate eqn. (20) will be essentially the same as eqn. (18) obtained in this work.

The correlation between fractionation factor  $\phi'(\text{SH})$  and the deuterium isotope mol fraction of solvent water can also be expressed by means of a relative fractionation factor  $\phi_r(\text{SH})$ , defined by eqn.

Table 6. Relative fractionation factor  $\phi_r(\text{SH})$  with different values for the deuterium isotope mol fraction of water,  $x(\text{D};\text{L}_2\text{O})$ , when  $K(\text{HDO})^2 = 3.76$ .

$x(\text{D};\text{L}_2\text{O})$	$\phi_r(\text{SH})$	$x(\text{D};\text{L}_2\text{O})$	$\phi_r(\text{SH})$	$x(\text{D};\text{L}_2\text{O})$	$\phi_r(\text{SH})$
0.10	0.9937	0.40	0.9755	0.70	0.9578
0.20	0.9875	0.50	0.9695	0.80	0.9519
0.30	0.9815	0.60	0.9636	0.90	0.9460

$$\phi_r(\text{SH}) = \frac{\phi'(\text{SH})}{\phi_0(\text{SH})} = \frac{\frac{1}{2}x(\text{HDO})}{x(\text{H}_2\text{O})} \times \frac{1-x(\text{D};\text{L}_2\text{O})}{x(\text{D};\text{L}_2\text{O})} \quad (21)$$

(21) as reported by Gold.<sup>13</sup>  $\phi_0(\text{SH})$  is the limit value for the fractionation factor  $\phi'(\text{SH})$  when  $n(\text{D};\text{L}_2\text{O})/n(\text{H};\text{L}_2\text{O}) \rightarrow 0$ . The value of  $\phi_r(\text{SH})$  at different deuterium isotope mol fractions of water can be calculated from eqn. (21) using the values from Table 5 for  $x(\text{H}_2\text{O})$  and  $x(\text{HDO})$ . The values for  $\phi_r(\text{SH})$  are listed in Table 6. A good linear correlation (22) was found to exist between the relative fractionation factor  $\phi_r(\text{SH})$  and the deuterium isotope mol fraction of water, when the method of linear least squares was applied to the values in Table 6. Because the relative fractionation factor is independent of the size of the fractionation factor itself, eqn. (22) presents the dependence of the

$$\phi_r(\text{SH}) = [-0.0595(2)]x(\text{D};\text{L}_2\text{O}) + 0.9994(1) \quad (22)$$

$(r = -0.99997)$

fractionation factor of any substrate of type SH on the deuterium isotope mol fraction of water. Only if the PGM were to be valid for the isotope disproportionation reaction of water, *i.e.*, if  $K(\text{HDO})^2 = 4$ , the experimental fractionation factor  $\phi'(\text{SH})$  would be constant over the whole range of  $x(\text{D};\text{L}_2\text{O})$ . The dependence of  $\phi'(\text{SH})$  upon the deuterium isotope mol fraction of water, when  $K(\text{HDO})^2 = 3.76$ , is illustrated in Fig. 1. When  $x(\text{D};\text{L}_2\text{O})$  is expressed in terms of the mol fractions of the different water species, and eqn. (5) is applied to eqn. (21), an expression (23) is obtained for the relative fractionation factor  $\phi_r(\text{SH})$ . Also the relative fractionation factor  $\phi_r(\text{SH})$  would be independent of the deuterium isotope mol fraction of water only if  $K(\text{HDO})^2$  had its statistical value of 4. As can be seen from eqn. (23), the value of  $\phi_r(\text{SH})$  would be unity

$$\phi_r(\text{SH}) = \frac{1}{2} \frac{K(\text{HDO})^2 x(\text{D}_2\text{O}) + 2x(\text{HDO})}{2x(\text{D}_2\text{O}) + x(\text{HDO})} \quad (23)$$

over the whole range of  $x(\text{D};\text{L}_2\text{O})$ . The value of  $1 - \phi_r(\text{SH})$  at  $x(\text{D};\text{L}_2\text{O}) = 1$  presents the error that can be introduced in the measurements of the fractionation factors if the deviations from the PGM are neglected.<sup>18</sup> From eqn. (22) a value of 0.94 can be calculated for  $\phi_r(\text{SH})$  with  $x(\text{D};\text{L}_2\text{O}) = 1$ , and thus the error will be about 6%.

In summary, the experimental results obtained in this work support the view that at present the use of

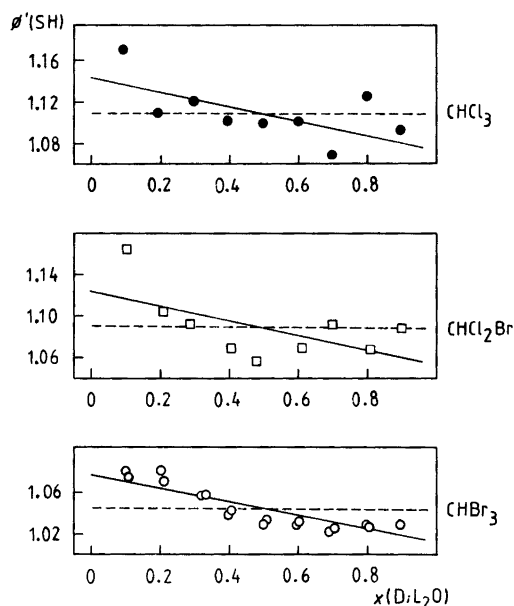


Fig. 1. Dependence of fractionation factor  $\phi'(\text{SH})$  upon the deuterium isotope mol fraction of water,  $x(\text{D};\text{L}_2\text{O})$ , when  $K(\text{HDO})^2 = 3.76$ . The fractionation factors  $\phi'(\text{SH})$  for drawing the unbroken straight lines were calculated using the  $\phi_r(\text{SH})$  values from Table 6 so that each  $\phi'(\text{SH})$  at  $x(\text{D};\text{L}_2\text{O}) = 0.5$  was to be the mean value of the experimental fractionation factors measured for the trihalomethanes (Tables 1, 2 and 3). The broken lines for  $\phi'(\text{SH})$  represent the situation if the PGM were to be valid for the disproportionation reaction of water, *i.e.* if  $K(\text{HDO})^2 = 4$ .

the PGM in the isotope disproportionation equilibrium of water provides a good approximation in the treatment of solvent isotope effects in mixtures of H<sub>2</sub>O and D<sub>2</sub>O. The exact value of the equilibrium constant becomes important if the experimental accuracy is essentially improved. It seems, however, that if the fractionation factor measurements with substrates of type SH are carried out at either end of the range of deuterium isotope mol fraction of water, they should be corrected.

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